

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-192937

(43)Date of publication of application : 29.07.1997

(51)Int.Cl.

B23H 9/00

(21)Application number : 08-005560

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(22)Date of filing : 17.01.1996

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(54) SURFACE TREATING METHOD BY SUBMERGED ELECTRIC DISCHARGE

(57)Abstract:

PROBLEM TO BE SOLVED: To form a deposited layer having strong adhesive force on the front surface of an iron steel, a cemented alloy, or the like by using a material in which the powder containing metal halide compound powder is formed as a discharge electrode, and generating electric discharge between the electrode and a work piece in liquid in which carbon exists.

SOLUTION: A submerged electric discharge deposited front surface by a TiH₂ powder electrode is composed of Ti and TiC and bonded to a cemented alloy front surface of a base material without containing any oxide. In the reaction with the base material surface in electric discharge, since the temperature of the cemented front surface instantaneously reaches the boiling point of the material, the deposited Ti and TiC can be diffused and fused to the base material side. The component composition from the boundary surface to the base material to the front surface of the deposited layer is Ti and TiC, and the boundary surface and the front surface are bonded without containing any oxide. This Ti component of the topmost front surface part of the deposited layer is oxidized in the air into TiO₂, however, the inside is Ti with activity.

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[JP,09-192937,A(1997)]

Japanese (PDF)

File Wrapper Information

CLAIM + DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS
DRAWINGS

[Translation done.]

Drawing selection Representative drawing

摩擦摩耗試験結果

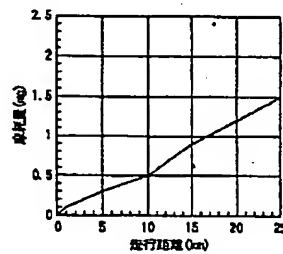
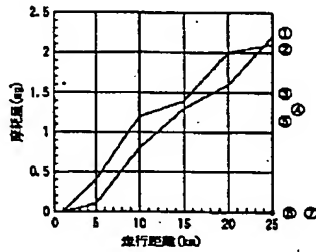
(a) 放電 (超硬材 GTI30)

(b) イオンミキシング (超硬材 GTI30)

TiN + Ti2N 膜厚 2 μm

硬度 HV3500 程度

— Ion - mixing



- ①② 研削加工した未処理表面
 ③④⑤ Ti 金属電極による放電処理によるもの
 ⑥ TiH_2 圧粉体電極による放電処理によるもの
 ⑦ TiH_2 + TiB_2 圧粉体電極による放電処理によるもの

摩耗試験条件

摩耗試験 (大針式ピンディスク方式)

ピン形状: 7.98mm ϕ (0.5cm)押付け力: 0.5kgf によって押付け圧力 1kgf/cm²

摩擦速度: 1m/s

ディスク材: SK-3

雰囲気: 大気中

[Translation done.]

Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the NCIP, and those who drafted this document in the original language are not responsible for the result of the translation.

Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

Translated: 00:52:39 JST 11/24/2004

Dictionary: Last updated 10/12/2004 / Priority:

CLAIMS

[Claim(s)]

[Claim 1] The surface treatment method by the discharge among liquid characterized by generating discharge between the above-mentioned electrode and a workpiece in the liquid with which carbon exists, using as a discharge electrode what fabricated the powder containing metal hydride powder, and forming the surface layer containing the compound of the above-mentioned metal on the above-mentioned workpiece surface.

[Claim 2] What fabricated the powder containing metal hydride powder is used as a discharge electrode. The surface treatment method by the discharge among liquid characterized by generating discharge between the above-mentioned electrode and a workpiece in the liquid with which the polymeric materials which pyrolyze and produce carbon exist, and forming the surface layer containing the compound of the above-mentioned metal on the above-mentioned workpiece surface.

[Claim 3] Claim 1 or 2 -- the surface treatment method by the discharge among liquid characterized by the metals contained in an electrode as hydride being transition metals in the surface treatment method by discharge given in either among liquid.

[Claim 4] What mixed and fabricated other metals, carbide, a nitride, and way ghost powder to metal hydride powder is used as an electrode of discharge among liquid. The surface treatment method by the discharge among liquid characterized by generating discharge between the above-mentioned electrode and a workpiece in the liquid with which carbon exists, and forming the surface layer containing the compound of higher hardness on the above-mentioned workpiece surface.

[Claim 5] What mixed and fabricated other metals, carbide, a nitride, and way ghost powder to metal hydride powder is used as an electrode of discharge among liquid. The surface treatment method by the discharge among liquid characterized by generating discharge between the above-mentioned electrode and a workpiece in the liquid with which the polymeric materials which pyrolyze and produce carbon exist, and forming the surface layer containing the compound of higher hardness on the above-mentioned workpiece surface.

[Claim 6] Claim 2 or 5 -- the surface treatment method by the discharge among liquid

characterized by the polymeric materials which pyrolyze and produce carbon being mineral oil fat or vegetable fat and oil in the surface treatment method by discharge given in either among liquid.

[Claim 7] Claim 1 or 6 -- [either] in the surface treatment method by discharge of a description among liquid The surface treatment method by the discharge among liquid characterized by fabricating one sort or the thing compounded and added to an electrode material, using the powder of zircon, vanadium, niobium, and a tantalum for it as an electrode, generating discharge between this electrode and a workpiece, and forming a high toughness surface layer on the above-mentioned workpiece surface.

[Claim 8] Claim 1 or 7 -- the surface treatment method by the discharge among liquid characterized by fabricating what added a workpiece and metal powder of the same kind to either in the surface treatment method by discharge of a description among liquid, using as an electrode, generating discharge between this electrode and a workpiece, and improving the description of the surface of the above-mentioned workpiece.

[Claim 9] Claim 1 or 7 -- the surface treatment method by the discharge among liquid characterized by performing secondary elaboration using a non-consumable electrode, and raising the physical properties of the above-mentioned surface layer after forming a surface layer in the workpiece surface by the surface treatment method by discharge given in either among liquid.

[Claim 10] The surface treatment method by the discharge among liquid characterized by a non-consumable electrode being in any of graphite, copper, a tungsten, a silver tungsten, a copper tungsten, and the tungsten carbide in the surface treatment method by discharge among liquid according to claim 9.

[Claim 11] Claim 1 or 10 -- the surface treatment method by the discharge among liquid characterized by a workpiece being a nonferrous metal in the surface treatment method by discharge given in either among liquid.

[Claim 12] Claim 1 or 10 -- the surface treatment method by the discharge among liquid characterized by a workpiece being superalloy in the surface treatment method by discharge given in either among liquid.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the technique which carries out deposition coating of the remarkable high ingredient of wear-resistant or corrosion-resistant on a metallic material or a conductive ceramic material at the radical of a high degree of adhesion, and relates to the surface treatment technique of giving the above-mentioned property excellent in metal mold, the tool, or the machine part.

[0002]

[Description of the Prior Art] The technique of carrying out deposition coating of the surfaces, such as a metallic material, and giving corrosion resistance and abrasion resistance by discharge among liquid is well-known in patent application already being done by us. The main point of those techniques that became well-known is as follows.

(1) The electrode which mixed and pressed the powder of WC and Co performs discharge among liquid. Once performing deposition processing at this time, it is the method of performing a remelting electron discharge method and acquiring a higher degree of hardness and high adhesion with another electrode (for example, a copper electrode, a graphite electrode).

(2) It is the discharge-among liquid surface treatment method to which a lifting and Ti serve as TiC (titanium carbide), serve as matter of higher hardness extremely, and carry out deposition coating of carbon and the high-temperature-chemistry reaction which working liquid pyrolyzes and generates like titanium (henceforth, Ti). At this time, the metal which can serve as a binder like Co (cobalt) is **-ized in a compression-molding ingredient.

[0003] Conventional technology is hereafter explained using drawing 1. A processed ingredient (base material S50C) is made to accumulate by performing an electron discharge method in liquid using the mixed green compact electrode of WC-Co (tungsten carbide-cobalt) (primary processing). Subsequently, an electrode like a copper electrode which is not exhausted so much performs remelting processing (secondary elaboration). With deposition of primary processing, the degree of hardness was also Hv=1410 intensity, and there were many cavities among organizations, and by remelting processing of secondary elaboration, the cavity of an enveloping layer is lost and the degree of hardness is also improving with Hv=1750. (Drawing 2)

[0004] These methods are well deposited on the radical of a high degree of adhesion to steel, and a degree of hardness high about 50% is shown rather than the sintering cemented carbide of WC+Co of the same component, or TiC+Co. For example, although the degree of hardness of the usual cemented carbide tool of WC70 and Co30 is Hv=850-950, in the electron discharge method treating surface of the cemented carbide which consists of the same component as this, it is after termination of secondary elaboration, and is Hv=1710.

[0005] However, in the conventional method, it is difficult for the surface of a sintered material like the nature alloy cutting tool of superhard to form an enveloping layer with the firm adhesion force, and there is big variation also in the bond strength of an enveloping layer further.

[0006] Although conventional technology deposits an enveloping layer on the steel surface well, the Reason which cannot deposit an enveloping layer firmly is explained to the surfaces, such as cemented carbide. Here, since deposition coating by Ti and its mixture becomes the main items of this invention, suppose that these phenomena are described about Ti.

[0007] As for 1800 degrees C and the boiling point, the melting point of Ti is a metal of

3000 degrees C or more. In the state of being in the air, it is covered with the thin precise oxide layer (Ti-O₂) by ordinary temperature, and is chemically stable. This is like aluminum being covered with the precise oxide film aluminum 2O₃. Then, the following phenomena will be produced, if the powder of Ti is pressed and it is used as an electrode (henceforth a green compact electrode) of an electron discharge method. If discharge arises between an electrode surface and a processed side, a discharge point will turn into the boiling point of an ingredient, working liquid (mineral oil in this case) will cause heat-of-vaporization explosive decomposition simultaneously, and the matter of the discharge point which is an elevated temperature will disperse. The quality of debris the processed side of the workpiece of a counter electrode, among those is usually deposited. [about 50% of]

[0008] Discharge is generated although Ti forms the thin oxide layer in the air. This Reason is an object whose oxide layer of this is very thin, and is because it is easy to cause dielectric breakdown. If discharge generating occurs by dielectric breakdown, and takes high voltage or the short distance between electrodes is taken, the electric potential gradient (V/cm) produced between poles will become high, and it will result dielectric breakdown in lifting discharge generating. A high-tension-transmission line causes corona discharge, or if this is a thin oxide film, it will be understood also from tunnel current flowing. However, if a partner pole is contacted before discharge occurring, and molten metal's rising with a discharge pressure and separating from an electrode parent or a processed object parent, if the distance between electrodes is made small in order to make an electric potential gradient high in this way, the idle state of the discharge called short circuit between poles will happen. In short, the unstable phenomenon of an electron discharge method may happen. We have just already been going to experience that Ti electrode and Ti green compact electrode have an unstable electron discharge method.

[0009] In the carbon which working oil disassembled and generated by the time it deposited on the process, bombardment [this Ti], and the processed side and the surface was covered by the next bombardment, and hot titanium, a lifting and its part serve as TiC in a chemical reaction. In this case, when the bombardment [a processed ingredient tends to make Ti and an alloy like steel and / the melting point] to a comparatively low thing (for example, steel the melting point of 1560 degrees C, 2500 degrees C of boiling points) compared with cemented carbide etc., it deposits on a base material penetration or by adhering well.

[0010] It is as having stated to having existing applied that the cavity produced by the first deposition will be crushed by remelting, and high deposition coating of a consistency can be performed if an electrode polarity and discharge electrical-and-electric-equipment conditions are changed and secondary elaboration is performed with the same electrode or another electrode to what was deposited once. The microphotography of the organization by the layer (primary processing) and secondary elaboration which were deposited first is shown in drawing 2 by way of precaution.

[0011] However, even if a processed ingredient deposits what the aforementioned Ti

powder pressed to cemented carbide (WC+Co, sintered alloy of WC+Co+TiC) etc., most does not accumulate that it is very easy to exfoliate. In order to understand this, it is good to reason from the welding phenomenon of a metallic material. Arc welding is possible for steel etc. The cemented carbide comrade is impossible for arc welding. Moreover, the arc welding of cemented carbide, steel, etc. is also impossible. However, since it cannot weld when the material-side has oxidized also in the arc welding of steel, it has been common sense to use the flux of antioxidizing for an electrode or weld-line material. Moreover, even if the melting point is low like aluminum, there is what has difficult arc welding in the usual state. This is because the precise film of the thin aluminum oxide always generated and has covered in the air on the surface of aluminum, and it is known that it can weld if this is destroyed like supersonic vibration.

[0012] From the above welding phenomenon, the green compact electrode of Ti explains the Reason which is not deposited by bombardment on the surface of cemented carbide, either. Since the powder surface of Ti is covered by the thin oxide layer (TiO₂), it is thought that this has checked junction to a deposit and a parent metal. That is, since the rate of surface area becomes larger compared with the volume as grain size becomes small, the rate of occupying on the surface of an oxide will increase the powder of Ti. This is alike when the amount of the surface in welding which oxidized, or an adhering oxide is made to act remarkably greatly. This is shown below.

[0013] It asks for the rate of the surface area of grain, and the volume.

(1) When it is assumed that grain is a ball Surface area $S = \pi \cdot d^2$ Volume of grain $V = \pi \cdot d^3 / 6$ (however, d diameter of grain)

Ratio of surface area to the volume When it is assumed that $S/V = 6/d$ (2) grain is a cube Surface area $S = 6 \cdot d^2$ Volume of grain $V = d^3$ (however, d die length of one side)

Ratio of surface area to the volume The consideration more than $S/V = 6/d$ shows that the rate of surface area increases the more the more grain is small. The effect by an oxide film will be received from this, so that grain is small, when the surface is precisely covered with the oxide film etc. Moreover, cemented carbide is considered that that the melting point is also high makes weldbonding difficult. It is for a welding fusion zone to become difficult to flow if the melting point is high. On the other hand, with steel, a welding fusion zone flows easily.

[0014] In addition, if the above-mentioned surface oxide layer carries out from the view which it has of having checked fusion by deposition, the effect will increase, so that the effect of an oxide is great and the pressed fine particles have a fine grain size. Since the rate of occupying solid Ti titanium metal electrode on the surface of an oxidizing zone is small if compared with it, coating with a metal Ti electrode is possible although it is not efficient. Ti solid electrode is deposited quite well. Moreover, ***** deposits quite well Ti electrode which carried out the temporary-quenching join with a vacuum furnace etc. However, Ti solid electrode and Ti sintered electrode of alimentation (thickness) is also small, and the adhesion force is also less than the below-mentioned TiH₂. That is, the

hindrance factor of an oxide is considered with since it remains.

[0015]

[Problem to be solved by the invention] In the surface treatment method using the conventional electron discharge method so that clearly from the above explanation Since the oxide film (TiO_2) which has covered the surface precisely exists in the case of the electrode which pressed fine particles, such as Ti, even if oxygen dissociates at the time of discharge, the fine-particles metal which constitutes an electrode is considered to deposit on a processed side or to have prevented uniting with a partner metal. Furthermore, bombardment [temperature / a processed side] with TiO_2 more often when an electrode object disperses by a discharge pressure since the pyrolysis temperature of TiO_2 is an elevated temperature very much (1800 degrees C). Moreover, since it does not come out so much and the distance between electrodes of discharge generating becomes narrow, while the short circuit in processing increases and degrading a processed surface (since it is hard to generate discharge for an oxide film), it is thought that machining efficiency is checked.

[0016] Also as opposed to a thing like sintering cemented carbide made in order that this invention might solve the above-mentioned technical problem It deposits well, and moreover, the adhesion force is firm, further, it hardly generates but the short circuit in processing also offers the surface treatment method by an electron discharge method also with high machining efficiency and beautiful ***** surface roughness.

[0017]

[Means for solving problem] The surface treatment method by discharge of the 1st invention among liquid generates discharge between the above-mentioned electrode and a workpiece in the liquid with which carbon exists, using as a discharge electrode what fabricated the powder containing metaled hydride powder, and forms the surface layer containing the compound of the above-mentioned metal on the above-mentioned workpiece surface.

[0018] [the surface treatment method by discharge of the 2nd invention among liquid] Discharge is generated between the above-mentioned electrode and a workpiece in the liquid with which the polymeric materials which pyrolyze and produce carbon exist, using as a discharge electrode what fabricated the powder containing metaled hydride powder, and the surface layer containing the compound of the above-mentioned metal is formed on the above-mentioned workpiece surface.

[0019] The surface treatment method by discharge of the 3rd invention among liquid uses transition metals for the metal contained in an electrode as hydride in either the 1st invention or the 2nd invention.

[0020] [the surface treatment method by discharge of the 4th invention among liquid]

Discharge is generated between the above-mentioned electrode and a workpiece in the liquid with which carbon exists in metaled hydride powder using what mixed and fabricated other metals, carbide, a nitride, and way ghost powder as an electrode of discharge among

liquid, and the surface layer containing the compound of higher hardness is formed on the above-mentioned workpiece surface.

[0021] [the surface treatment method by discharge of the 5th invention among liquid] What mixed and fabricated other metals, carbide, a nitride, and way ghost powder to metaled hydride powder is used as an electrode of discharge among liquid. Discharge is generated between the above-mentioned electrode and a workpiece in the liquid with which the polymeric materials which pyrolyze and produce carbon exist, and the surface layer containing the compound of higher hardness is formed on the above-mentioned workpiece surface.

[0022] The surface treatment method by discharge of the 6th invention among liquid uses mineral oil fat or ***** for the polymeric materials which pyrolyze and produce carbon in either the 2nd invention or the 5th invention.

[0023] [the surface treatment method by discharge of the 7th invention among liquid] In the 1st or the 6th one of invention, fabricate one sort or the thing compounded and added to an electrode material, and powder, such as zircon, vanadium, niobium, and a tantalum, is used for it as an electrode. Discharge is generated between this electrode and a workpiece and a high toughness surface layer is formed on the above-mentioned workpiece surface.

[0024] The surface treatment method by discharge of the 8th invention among liquid fabricates what added a workpiece and metal powder of the same kind, it is used for it as an electrode, it generates discharge between this electrode and a workpiece, and the description of the surface of the above-mentioned workpiece is made to improve in the 1st or the 7th one of invention.

[0025] After the surface treatment method by discharge of the 9th invention among liquid forms a surface layer in the workpiece surface by the 1st or the 7th one of invention, it performs secondary elaboration using a non-consumable electrode, and it is made to raise the physical properties of the above-mentioned surface layer.

[0026] The surface treatment method by discharge of the 10th invention among liquid uses for a non-consumable electrode any of graphite, copper, a tungsten, a silver tungsten, a copper tungsten, and the tungsten carbide they are in the 9th invention.

[0027] The surface treatment method by discharge of the 11th invention among liquid uses a nonferrous metal for a workpiece in the 1st or the 10th one of invention.

[0028] The surface treatment method by discharge of the 12th invention among liquid uses superalloy for a workpiece in the 1st or the 10th one of invention.

[0029]

[Mode for carrying out the invention]

Suppose that the feature operation effectiveness at the time of using as an electrode which pressed gestalt 1.TiH₂ of implementation of invention is described. At the temperature of 300 degrees C or more, as for TiH₂, hydrogen begins secession. Since it is thought that the surface of a discharge point is in the boiling point of the ingredient, time amount (usually 0.1

microsecond - 1000 microseconds) after discharge begins until it ends decomposes TiH_2 thoroughly. Ti and the decomposed hydrogen assume a chemical reaction with very strong activity in that case. That is, a hydride like TiH_2 is an unstable compound, and even if it says from the common sense of a chemical change, it causes the high reaction of activity. That is, when hydrogen of a nascent state strikes the processed surface, there is an operation which removes the oxide film (the oxide etc. exists except for whether the surfaces, such as cemented carbide and steel, are precise) which exists in the surface (cleaning).

[0030] Moreover, since bombardment [Ti / without completely including an oxide / with activity having / a processed side], it can deposit with high adhesion. And since TiH_2 is the matter weak originally, it is made detailed according to discharge generating, and it is considered to become finer than the grain size of TiH_2 original. Therefore, when it is processed on the same electrical-and-electric-equipment conditions, good machined surface granularity is obtained rather than based on the conventional WC-Co green compact. 6-12micromRmax is conventionally obtained to 30-40micromRmax.

[0031] And [a state] although the state of the beginning of a processed side is the processed metallic material cleaned from hydrogen of the nascent state. Once a processing part takes a round of the surface and coating is briefly carried out by Ti or TiC , it will become the surface of Ti or TiC (based on combination with carbon by an oil-content solution) from a degree, but the particles covered by Ti which contains TiO_2 like before will not exist in this at all. Therefore, coating performed from a degree also serves as a deposit where adhesion is very high. For this reason, it became clear that remarkable high adhesion was shown also to cemented carbide, and the epoch-making abrasion resistance which was not conventionally obtained in the abrasion test was shown.

[0032] In addition, it is thought that it will stick if a discharge point reaches in an electron discharge method till the boiling point of an ingredient in ordinary arc welding although welding of cemented carbide is impossible, and it is cleaned as mentioned above, since the energy density is moreover several 100 times high compared with arc welding etc.

[0033]

[Working example]

The powder of 10 or less microseconds of grain size of example 1. TiH_2 is pressed on condition of following.

diameter: -- 15mm, load: -- 11.4t (about 6500kg/cm²) and thickness: -- this is pasted up on a copper rod with electroconductive glue about 5mm, and it is used as an electric discharge machining electrode. Processing is based only on primary processing. To a processed ingredient and cemented carbide (WC+ TiC +Co:GTi30 MITSUBISHI MATERIALS), the electron discharge method was performed on condition of following, and the deposit was formed in the surface.

(1) Processing conditions, a degree of hardness, machined surface granularity, abrasion test result 1 processing-conditions: discharge current $I_p=3.5A$, pulse width $\tau_{pu} = 32-$

microsecond and floor-to-floor-time = 2 minutes, a green compact electrode polarity (-)

2) A degree of hardness, machined surface granularity: Vickers hardness Hv = 600-900 (measuring pressure of 10g), deposit thickness 13 micrometers, machined surface granularity 10micromRZ3 abrasion-test (large ** type pin disk method) result: Atmosphere The inside of atmospheric air, pin configuration $\phi 7.98\text{mm}$ (0.5cm^2) Force with push 0.5Kgf, embossing pressure force 1 Kgf/cm² friction velocity 1m/[s and], disk material The abrasion loss of 0mg was obtained in SKH-3 and 25km of abrasion test runs.

[0034] In addition, it is as follows when abrasion loss is shown about a superhard ingredient for the comparison of an abrasion test result.

The abrasion loss of the cemented carbide (GTi30) which ground the surface :2.1mg Discharge coating treatment side by a titanium metal electrode : 0.7-1.5mg TiN+Ti2N (2 micrometers of thickness) ion mixing processing side: 1.5mg (notes) (considered the resolution of 0.1mg of abrasion loss Measurement Division)

The above result is shown in drawing 3 . The degree of hardness Hv obtained here = although 600-900 is quenching steel or only the annealed steel intensity, the abrasion resistance is remarkably high. Although the degree of hardness of the cemented carbide of a base material is as high as 1500 to Hv=1800 intensity, as the above-mentioned result shows, it is worn out no less than 2.1mg in the cemented carbide which ground the surface.

[0035] (2) the consideration 1 to abrasion resistance having improved remarkably -- although a degree of hardness is low in this way, analysis clear about the point which says that abrasion resistance is high at present has not been performed, but artificers think as follows. The discharge-among liquid deposition surface by a TiH₂ fine-particles electrode is composed from Ti and TiC, and it has stuck the cemented carbide surface of a base material, without completely including an oxide. Diffusion fusion of Ti and TiC which deposited the reaction at the time of discharge with a base material side since the superhard surface also became by the boiling point of the ingredient momentarily can be carried out to some extent at the base material side. The component composition from an interface with a base material to the surface of a deposit (in this case, about 13 micrometers) is also Ti and TiC, and it has stuck, without completely including an oxide. Although the best surface section of a deposit oxidizes in mind and this Ti component serves as TiO₂, the interior serves as Ti [having had activity].

[0036] Therefore, when the abrasion test was done and disk material (SK-3) is contacted, after wear clearance of the best surface section is carried out, disk material unites with the Ti deposit side, and is removed, and it is thought that adhesion transfer is carried out in the direction of the processed surface. Since TiC also exists in the processed side from the first, I think that the disk material (SK-3) which carried out adhesion transfer of a little soft Ti surface is carrying out adhesion protection.

[0037] 2) When it considers as mentioned above, you have to describe the point of

difference in the adhesion of an electroplating side, and logic with decomposition hydrogen of the working liquid by discharge. Also in electroplating, a plated metal deposits to cathode. In that case, the adhesion of plating is not high although the cathode face should also be cleaned by hydrogen of the nascent state by disassembly of a plating water solution. It is known that a base material and a plated surface will become weak by hydrogen embrittlement rather. Although plating may also be cleaned [the surface], since it is not elevated-temperature high voltage, a plated metal may consider this because fusion diffusion cannot be carried out to a base material.

[0038] 3) Moreover, when working oil decomposes by an electron discharge method, it is divided into carbon and hydrogen, and since a lot of carbon deposits, the anode plate side is saying whether does hydrogen bombardment cathode and it will clean. This operation cannot be disregarded. When the green compact of WC+Co is made surely to deposit on the steel surface, the high deposit of remarkable adhesion has been obtained. However, high adhesion was not acquired even if you were going to make it deposit this on the cemented carbide surface. Moreover, even if it was going to make steel accumulate with the green compact electrode of mere titanium powder, the conditions deposited well were not able to be found out. From such an experimental result, from the hydrogen decomposed by discharge among liquid, since deposition in cemented carbide was impossible, although the surface is covered with the oxide film like titanium powder, it is thought that its reducing action is impossible.

[0039] The experimental result by the TiH₂ green-compact electrode at the time of changing example 2., next discharge electrical-and-electric-equipment conditions is shown. Processing is based only on primary processing.

(1) When an electrode polarity is changed, the green compact process condition of TiH₂ is 1 green compact electrode polarity (-) like an example 1.

Discharge current I_p = it is degree-of-hardness $H_v=670-900$ on the surface of processed (measuring pressure of 10g) at the time of A [10] and pulse width $\tau_{up}=32$ -microsecond floor-to-floor-time = 5 minutes.

2) Green compact electrode polarity (+)

It is degree-of-hardness $H_v=1450-1550$ on the surface of processed (measuring pressure of 10g) at electric conditions same as the above.

A degree of hardness also changes by polar change from the above-mentioned 12.

[0040] (2) When the discharge current is enlarged and pulse width is made very small, they are discharge current $I_p=45A$, pulse width $\tau_{up}=0.5$ -microsecond floor-to-floor-time = 2 minutes, and a green compact electrode polarity (-).

The degree of hardness H_v on the surface of processed = 2000-3000 (measuring pressure of 10g)

The degree of hardness H_v on the surface of processed = 1300-2000 (measuring pressure of 50g)

Deposition thickness 2 micrometers, machined surface granularity When 6micromRz

measuring load is small, it is degree-of-hardness size, and it is saying that becoming somewhat soft in load size has the inclination the surface being hard and the interior being somewhat soft, and lopsidedness will be formed in hardness. This is strengthened to thermal expansion, an impact, etc. in the case of practical use.

[0041] (3) The processing process which the surface is hardened remarkable, and makes soft enough as it goes into the interior, makes the means which raises lopsidedness remarkably, makes first the conditions of 1. of the above (1), and then is made into the conditions of (2) from the result of the above (1) and (2) exists. Or there are methods, such as changing an electrode polarity into (+) and (-).

[0042] The experimental result of the discharge surface treatment to steel by the green compact electrode of example 3. TiH₂ is shown.

(1) Discharge surface treatment (only primary processing) was performed to steel (SK-3) on the same conditions as an example 1 using the green compact electrode of TiH₂.

The degree of hardness Hv of discharge current $I_p=3.5A$ and the pulse width $\tau_{\text{aup}}=32\text{-microsecond}$ floor-to-floor-time = 5-minute processed surface = 900-1000 (measuring pressure of 10g)

Deposition thickness The result of having performed secondary elaboration with the graphite electrode is shown in steel (SK-3) after a treatment process on condition of (1) of abrasion loss of 0mg (2) above-mentioned example 3. of 47 micrometers and an abrasion test result. Secondary elaboration conditions are the polarities (-) of discharge current $I_p=3.5A$, pulse width $\tau_{\text{aup}}=4\text{-microsecond}$ floor-to-floor-time = 5 minutes, and a graphite electrode.

degree-of-hardness $H_v=1600\text{-}1750$ of a processed side -- this shows that the degree of hardness is rising remarkably, if secondary elaboration is performed. What performed secondary elaboration by the copper electrode, the degree of hardness rose similarly.

[0043] This Reason is in the state which new Ti or new TiC does not deposit by secondary elaboration, and is because the rate that C which working oil decomposed and produced combines with the remains Ti in an enveloping layer, and TiC in an enveloping layer occupies increases.

[0044] The example using the green compact electrode which mixed other metals, carbide, the nitride, and the way ghost to gestalt 2. TiH₂ of implementation of invention is shown.

The metal which can become carbide by discharge among (1) liquid in order to extend further the outstanding property of the above which TiH₂ has (example: Ta, Nb, V, Zr)

(2) Carbide (example: TiC, TaC, NbC, VC, BC, B₄C)

(3) Nitride (example: TiN, hBN, CBN)

(4) Way ghost (example: TiB₂, way acid H₂B O₃, way sand Na₂B 4O₇.10 H 2O)

(5) Yttria (Y₂O₃)

Many experiments which were mixed to TiH₂ and formed the green compact electrode were conducted. As an example of representation in it, the thing of TiB₂ mixing, the thing of mixing of TiN, and the thing that doubled TiB₂ and TiN and was mixed are shown.

[0045] [only in primary processing] although a degree of hardness is more than cemented carbide When the graphite electrode (electrodes, such as copper and a tungsten, are sufficient) etc. performed secondary elaboration, it turned out that it has the lopsidedness which says that a degree of hardness improves further, the surface is set to one half of diamonds (equivalent to CBN 5000 or more Hv(s)), and the interior becomes soft.

[0046] Example 4.

Electrode material: TiH₂+TiB₂ (7:3 bulk densities)

When green compact application-of-pressure conditions etc. are the same as an example 1 and only primary processing is performed, in floor-to-floor-time = 5 minutes, electric condition: Ip=5.5A and tau=32microsecond 1) Degree-of-hardness:Hv=1850-2500 (10g of loads), thickness: -- 24-28 micrometers and degree-of-hardness: -- Hv=1650-2500 (50g of loads) was obtained.

As a result of doing an abrasion test for this like an example 1, the abrasion loss of the processed side was 0mg. Moreover, electrodischarge treatment of the addressing above was performed to the rake face of a carbide bit (MITSUBISHI MATERIALS UTi20), and the before flank for 2 minutes, respectively, the cut examination with an engine lathe was done, and the adaptability to the cutting tool was investigated. As a result, compared with what does not carry out electrodischarge treatment on the following cutting condition, the 1.9-time-as many longevity life as this was shown.

[0047] Moreover, electric condition: Ip=8A, tau = floor-to-floor-time = 5 minutes showed the 2.8-time-as many longevity life as this for 8 microseconds compared with what does not carry out electrodischarge treatment on the following cutting condition.

Cutting condition: Material to be cut S45C, slitting 0.5mm delivery 0.3 mm/rev, Cutting speed 160 m/min dry-cutting life judging: Wear width of the before flank in 7km of cutting distances (generally shown as VB)

[0048] 2) Electric condition: Ip=3.5A, tau=4microsecond, floor-to-floor-time =5 minute degree-of-hardness:Hv which were processed on the following electric conditions for 5 minutes with the graphite electrode after the above-mentioned primary processing = 2100-5100 (10g of loads), a green compact electrode (-) 1500-3000 (50g of loads), the Hv=32-36-micrometer degree of hardness Hv in thickness = calling it 5000 ranks second to 10000 of a diamond, and it is equal to 5000 of CBN. the property which the surface is remarkably hard, shows the lopsidedness hardness distribution included in the interior which is alike, follows and becomes soft gradually also in this case, and combines surface hardness and toughness -- **** -- since it is, it is very useful.

[0049] Example 5.

Electrode material: TiH₂+TiN (7:3 bulk densities)

1) primary processing-conditions: -- electric condition: -- Ip=5.5A and tau -- p= 32 microseconds and floor-to-floor-time =5 minute degree-of-hardness:Hv=1050-1800 (10g of loads), Electrode (-)

Although it is not like TiB₂ mixing at the time only of primary operation, subsequently this has a high degree of hardness, when TiB₂ is mixed.

2) A degree of hardness when a graphite electrode performs secondary elaboration turns into 1700 to Hv=2300 intensity after the above-mentioned primary operation.

[0050] Example 6.

Electrode material: TiH₂+TiB₂+TiN (2:1:1)

1) The degree-of-hardness processing conditions only by primary processing are a floor-to-floor-time = 5-minute degree of hardness like an example 1. Hv = 2000-2300 (10g of loads)

Thickness When a graphite electrode performs 12-18-micrometer² secondary elaboration, processing conditions are a floor-to-floor-time = 5-minute degree of hardness like an example 1. Hv = 2550-6050 (10g of loads)

thickness since it will fall to Hv=1800 intensity if [take high 14-18 micrometer measuring load, and] 50gr(s) -- this -- lopsidedness -- **** -- it is in ** that it is.

[0051] It aims at raising abrasion resistance in the gestalt of the operation which more than gestalt 3. of implementation of invention described. By primary processing of TiH₂ green compact, even if a degree of hardness is not so high, because adhesion is remarkable and strong is thought, but the result which says that abrasion resistance is high is obtained.

When TiB₂ grade is furthermore added, antifriction is high at higher hardness. When a degree of hardness is too high and there is fear of a brittle fracture, in order to grant toughness, to add Nb, Ta or NbC, TaC, etc. is validated. (This is information known in the direction of the sintered carbide tool)

[0052] Although 900 and a degree of hardness do not rise by Hv=600-700 and V by Ta and Nb, since it is hard to be missing even if it hits the surface with a hammer etc., the result of having added Ta, Nb, and V to TiH₂ about 10%, and having processed it on the same conditions as an example 1 is expected for toughness to also improve. Thickness is also deposited in the state of 10-20 micrometers and stable processing in processing for 5 minutes.

[0053] With the cutting tool, since Nb, TaC, VC, etc. were validated because of the improvement in toughness to interrupted cutting, they were added by about 10% of bulk density also in this experiment. As a result, although it does not become not much high with 900 to Hv=1050 intensity, it is processing, deposits on 20-micrometer or more a thickness of about 30 micrometers in a stable state for 5 minutes, and is tough also to a stroke etc.

[0054] That the surface deposit of a higher degree of hardness can be obtained became whether to be ** by adding a simple substance or TiB₂, TiN, etc. on the basis of TiH₂, as more than gestalt 4. of implementation of invention stated. The Reason which TiH₂ sticks to a processed ingredient is because decomposed Ti is activated [the reducing action on the surface of deposition by the nascent hydrogen ion produced when a hydride decomposes by the term of the gestalt of implementation of invention as above-mentioned, and] extremely. Moreover, it also seems that it is acting that the contact effective area to a base material becomes large in order to become detailed, when Ti is discharge generating.

Furthermore, since the organization which deposited by detailed-ization of Ti becomes fine, there are machined surface granularity and the feature of being easy to become minute.

[0055] If this principle is extended, it can be used for surface treatment using a metal hydride. The hydride it is considered that can use it for surface treatment is as follows.

Since it experimented about ZrH_2 as ZrH_2 , VH , VH_2 , NbH , TaH , $FeTiH_2$, $LaNi_5H_6$, $TiMnH_2$, $NaBH_4$, among these an example, it states as an example 6: Zr is excellent in thermal resistance and corrosion resistance, and is used also for a reactor as a moderator of a thermal neutron. It is used for a cutting tool, a bearing, a heat engine heatproof wear part, a pump part, etc.

[0056] The powder of example 7. ZrH_2 is made into a green compact on the same conditions as an example 1 (compression-pressure 6,500 kg/cm²), and it is processed in $I_p=5.5A$ and $\tau_{aup}=32\text{microsecond}$ to steel SK-3, and deposits well in the state of very stable processing. By processing, although it is not higher hardness so much in 8-10 micrometers in thickness, and degree-of-hardness $H_v=660-690$, at least this shows high abrasion resistance for 5 minutes. If a graphite electrode etc. performs secondary elaboration when you need higher hardness, a degree of hardness will rise. As for the electric conditions at the time of performing secondary elaboration, degree-of-hardness $H_v=1350-2000-2350$ are obtained with a graphite electrode (-) $I_p=3.5A$ and $\tau_{aup}=4\text{microsecond}$.

[0057] Gestalt 5 of implementation of invention .. Although it is not necessary to be so high a degree of hardness, the wear-resistant high surface etc. may be needed for aluminum, zinc, or the steel (especially mild steel) surface. For example, if it is aluminum and is the antifriction part of an aluminum engine, and zinc, there is a case where he wants to add antifriction, so firmly about the surface of the metal mold with which the configuration is made from zinc, and the machine part currently made from mild steel. In such a case, if TiH_2 powder and the powder of the metal which needs surface treatment are mixed and used, the surface lining whose degree of hardness is higher than a base material with high adhesion force will be formed. The example by the green compact electrode of TiH_2 +aluminum is described on aluminum as an example.

[0058] The green compact electrode of the bulk density 3:7 of two pairs of aluminum die-casting ingredients TiH aluminum which contain the example 8. processed raw material Si 11% is used. Current $I_p=5A$, τ_{aup} = a degree of hardness is 400 to $H_v=600$ intensity at the time of about 32 microseconds, and the surface section also reaches $H_v=1400$ intensity at $I_p=20A$ and the time of about $\tau_{aup}=260\text{microsecond}$. The same result is obtained even if it processes to zinc by this electrode presentation.

[0059] There are some which are called alloy-proof [super-] (superalloy) into the gestalt 6. nonferrous metal of implementation of invention, and this ingredient is also the target of a discharge surface treatment technique. That is, the ingredient of Ti and 6%aluminum4%V has the tensile strength of about 100kg/mm², and is Vickers hardness $H_v=260$ intensity. The green compact electrode of ZrH_2 performed surface treatment to this, with area [two]

an electrode of 1.7cm, it was processed in $I_p=5.5A$ and $\tau_{ap}=32\mu s$, and degree-of-hardness $H_v=660-690$ and 10 micrometers in thickness have been obtained. In addition, if a graphite electrode performs fabricating, 1350 to $H_v=2000$ intensity is acquired. The discharge coat of this processing was carried out to the nickel-aluminum-Ti-Nb-Ta alloy, and the same result has been obtained.

[0060] In the above this invention, the superalloy (it is also called superalloy) with which a processed ingredient (matter which counters with an electrode and generates discharge) uses steel and special steel, cemented carbide, a cermet, aluminum and its alloy, zinc and its alloy, copper, a copper alloy, nickel, Co, etc. as a principal component is applicable. What is called a nonferrous material and a nonferrous alloy are also applicable.

[0061]

[Effect of the Invention] Like the above, a deposit with several micrometers which has the powerful adhesion force in the surfaces, such as steel and cemented carbide, - the thickness of 10 micrometers of numbers can be formed by forming a metal or hydrides, such as Ti, Zr, V, Nb, and Ta, as a green compact, and performing discharge among liquid. This deposit has remarkably good abrasion resistance. Moreover, machined surface granularity is also good compared with other examples (WC+Co) performed on the same electrical-and-electric-equipment conditions, and it becomes the granularity of $1/2 - 1/3$. Moreover, if TiB_2 , TiN, TiC, TaC, NbC, VC, etc. are mixed into the above-mentioned hydride in order to raise a degree of hardness, a degree of hardness can be raised further. If the metal of Ta, Nb, and V is added to a green compact component, toughness will improve. If secondary elaboration is performed by the graphite electrode or a copper electrode, a degree of hardness will rise from 50% or more to about 2 times.

[Translation done.]